Statistical models of diffusion and aggregation for coke formation in a catalyst pore

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Abstract

We simulated models of diffusion and aggregation in long pores of small widths in order to represent the basic mechanisms of coke deposition in catalysts' pores. Coke precursors are represented by particles injected at the pore entrance. Knudsen diffusion, which is usually expected inside the pores, is modeled by ballistic motion of those particles. The regime of molecular diffusion is also analyzed via models of lattice random walks biased along the pores. The aggregation at the surface or near previously aggregated particles was modeled by different probabilistic rules, accounting for the possibilities of more compact or more ramified deposits. In the model of Knudsen diffusion and in some cases of molecular diffusion, there is an initial regime of uniform deposition along the pore, after which the deposits acquire an approximately wedge shape, with the pore plugging near its entrance. After the regime of uniform deposition and before that of critical pore plugging, the average aggregation position slowly decreases with the number N of deposited particles approximately as $N^{-0.25}$. The apparently universal features of deposits generated by microscopic models are compared with those currently adopted in continuum models.

Key words: statistical models, diffusion, aggregation, coke, catalyst deactivation

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1 Introduction

Catalyst deactivation is a phenomenon of great economic impact on many industrial processes. One of the main causes of deactivation is coke formation, which consists in the deposition of significant amounts of carbonaceous residues onto the catalyst surface. These deposits reduce the activity of the catalyst because they block the active sites and distort the porous structure, thus reducing the diffusivities of the reactants [1,2]. The importance of this phenomenon motivated several theoretical studies [3,4,5], with the deactivation process being modeled at three different levels [3]: the active site, the catalyst particle (or pellet) and the reactor. The studies at the particle level are strategic for the design of new catalysts.

Although the morphology of intra-particle coke deposits is essential to understand catalyst deactivation, it is usually oversimplified in theoretical models. Symmetrical coke profiles along the pores are frequently adopted, even when a realistic pore connectivity is considered for representing the structure of the catalyst. In most works, uniform (flat) coke profiles along the pore are considered [6,7]. On the other hand, nearly 20 years ago, Mann and co-workers introduced models in which the coke deposits inside the pores grew with a wedge shape of constant slope, with a higher concentration at the pore entrance [4,8,9]. These models were motivated by observations of higher coke concentrations in the external surfaces of several catalysts [10,11], which is typical of systems with a parallel mechanism of coke formation [3]. The common feature of most previous models is that the shape of the deposits is defined a priori, independently of the particular features of the diffusion and reaction processes. However, the interplay between transport of the precursors, reactions and coke formation is a fundamental aspect for catalyst deactivation.

The aim of this work is to study the morphology of the deposits generated by a statistical model of diffusion and aggregation of a chemical species inside a catalyst pore. The shape of a deposit changes in time due to the diffusion-limited aggregation of residues. Two transport regimes and various aggregation conditions will be considered, in order to show the features of the deposits which do not depend on the details of the diffusion and aggregation processes. The model neglects the internal structure of the coke precursors (molecules or radicals), considering a single diffusing/aggregated species, called particle C, inside the pore. The transport is modeled by random walks, considering separately the cases of molecular diffusion and Knudsen diffusion. In the case of molecular diffusion, the possibility of a small diffusional bias along the pores is analyzed. Details of the bond formation are also simplified by considering simple stochastic rules for aggregation of the diffusing species. Depending on the stochastic rule, dense or ramified deposits are obtained. Computationally, these models are similar to those of diffusion-limited aggregation (DLA) [12],

which have applications to other fields, such as electro deposition [13,14]. From this point of view, the main differences are the restriction of transport processes to a long pore of finite width, the possibility of aggregating the diffusing species at the whole surface and the more complex probabilistic rules of aggregation.

Although we are not considering the details of a particular deactivation process, we will derive conclusions on the large length scale features of the deposits which are in qualitative agreement with some experimental results [10,11]. On the other hand, they disagree with some of the most frequent theoretical assumptions for the coke profiles in continuous models. Among the main conclusions, both for Knudsen diffusion and some cases of molecular diffusion with small bias along the pore (weak convection effects), we will show that the coke deposits approximately have a wedge shape and plugging occurs at the pore mouth, after a transient with uniform deposition. However, the coke concentration near the pore mouth increases in time much faster than the concentration inside the pore, in contrast to the assumption of a wedge shape of constant slope. It suggests that incorporation of diffusion-limited aggregation mechanisms for coking in models for real catalysts may be relevant for a reliable description of their behavior. Another possibility is the incorporation of the effective growth laws obtained here in continuous reaction-diffusion models which require a prior assumption of the (time-dependent) shape for the coke deposits.

This paper is organized as follows. In Sec. II we will present the models of diffusion and aggregation. In Sec. III we will discuss qualitative and quantitative properties of the coke profiles generated by those models. In Sec. IV we summarize the results and present our conclusions.

2   Models

In order to simplify the porous structure of the catalyst and focus on the shape of the coke deposits inside the pores, we will consider the diffusion and aggregation processes at isolated pores. Each pore is a semi-infinite slab with discretized positions, as shown in Fig. 1. Different values of the width W are considered and are expressed in lattice units. Such approximation was previously adopted in several models of diffusion, reaction and deactivation by coking [6,7,8,9].

The coke precursors are represented by particles C, which enter the pore at its left side (pore mouth $x = 0$). The initial vertical position of each incident particle is randomly chosen. These initial conditions apply to all diffusion and aggregation models considered in this work. to all It is assumed that particles
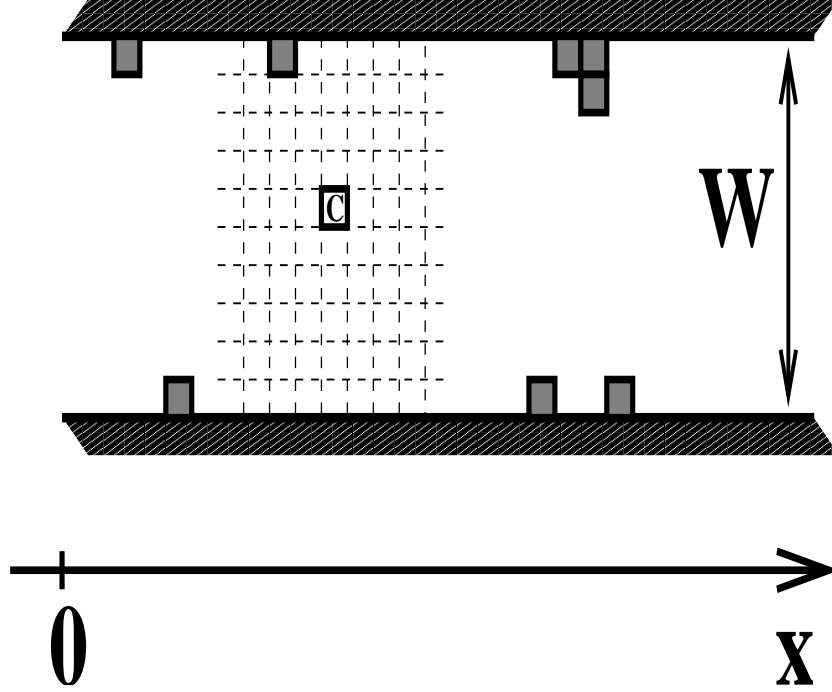
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Fig. 1. Long pore of width W with an internal square lattice structure and entrance at $x = 0$. The empty square is a diffusing particle C which moves on that network. Grey squares represent aggregated particles C.

C were produced not only inside the pore which is currently under study, but also in other regions of the reactor. Equivalently, it is being assumed that the deposit at a certain pore is mainly formed by residues produced elsewhere, which enter that pore through its opening.

The diffusion processes inside a pore will be simplified by restricting the positions of particles C, diffusing or aggregated, to the sites of an internal square lattice. Random walks on that network represent the molecular diffusion regime and ballistic motion represents Knudsen diffusion, as detailed below. Pore widths $W = 10$, $W = 20$ and $W = 40$ (measured in lattice units) were considered.

In Knudsen diffusion, the mean free path of molecules or radicals is much larger than the width of the pore. This low density regime inside a pore is typical of real catalytic processes. In our model, each C particle is released at $x = 0$ with velocity in a randomly chosen direction and executes ballistic motions between collisions with the pore walls or with the currently formed deposit (Fig. 2a). When the particle C encounters a pore wall or a previously aggregated particle, it may aggregate irreversibly at that position according to the probabilistic rules I or II, described below. If it does not aggregate, then it moves to a lattice site in its neighborhood with velocity chosen in a random direction and continues moving until colliding again. This random motion of a single particle is executed until it aggregates. After aggregation, a new particle

C is left at $x = 0$. Since the pore is very long, the number of particles C that leave it at the right side during the simulations is negligible.

The second regime considered here is that of molecular diffusion, in which the mean free path of a particle C is much smaller than the width of the pore. In this case, particles C execute biased random walks inside the pore (Fig. 2b), in which steps in the y direction (up or down in Fig. 2b) and in the negative x direction (left in Fig. 2b) are performed with rate 1, while steps in the positive x direction (right in Fig. 2b) are performed with rate u, with $u > 1$. Consequently, $v \equiv u - 1$ represents the intensity of the diffusional bias. This diffusion mechanism is supposed to describe the interaction of the particle C with the remaining molecules of the fluid which will not form the deposit and, consequently, do not need to be explicitly represented in the model.
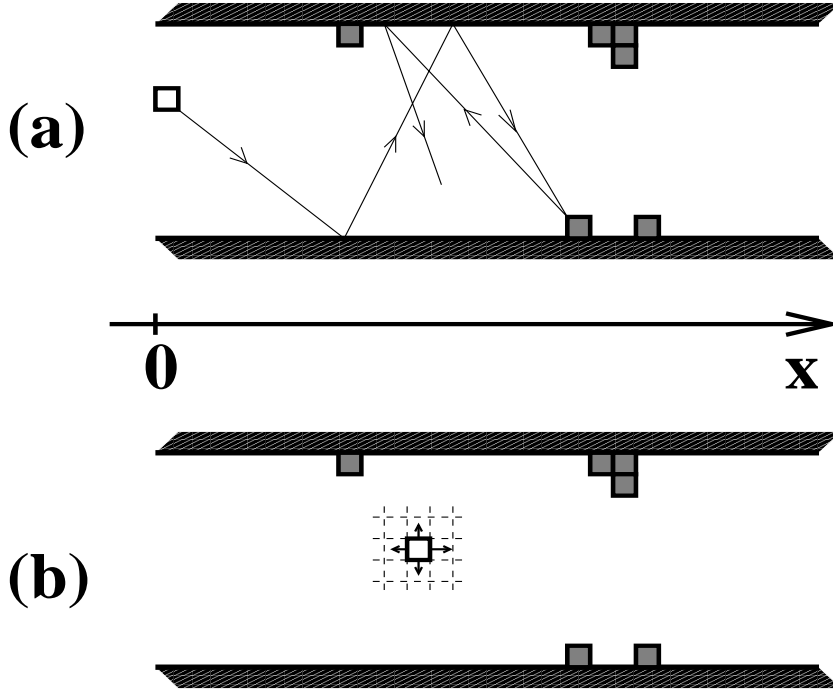

Fig. 2. (a) Illustration of the ballistic motion of a particle (empty square) inside a catalyst pore in the model of Knudsen diffusion. Velocity directions are random after collisions. Grey squares represent aggregated particles. (b) Illustration of the biased random walk of a particle (empty square) in the molecular diffusion model. The arrows indicate possible movements and their lengths illustrate the bias along the positive x direction.

Now we describe the aggregation rules, both of them considered in simulations of Knudsen and molecular diffusion. The sites at the pore walls and the previously aggregated C are treated equivalently as occupied sites. When a particle C is at a site with one or more occupied neighbors, it may aggregate irreversibly at that position with probability p_{ag}. Some possible aggregation positions are shown in Fig. 3, with the corresponding numbers of occupied nearest neighbors, n. It is expected that p_{ag} increases with n, but their rela-

tion strongly depends on the specific catalyst and coke precursor. Thus, since our aim is to investigate general features of coke deposits, we will consider two different aggregation rules with different functional dependences of p_{ag} on n.
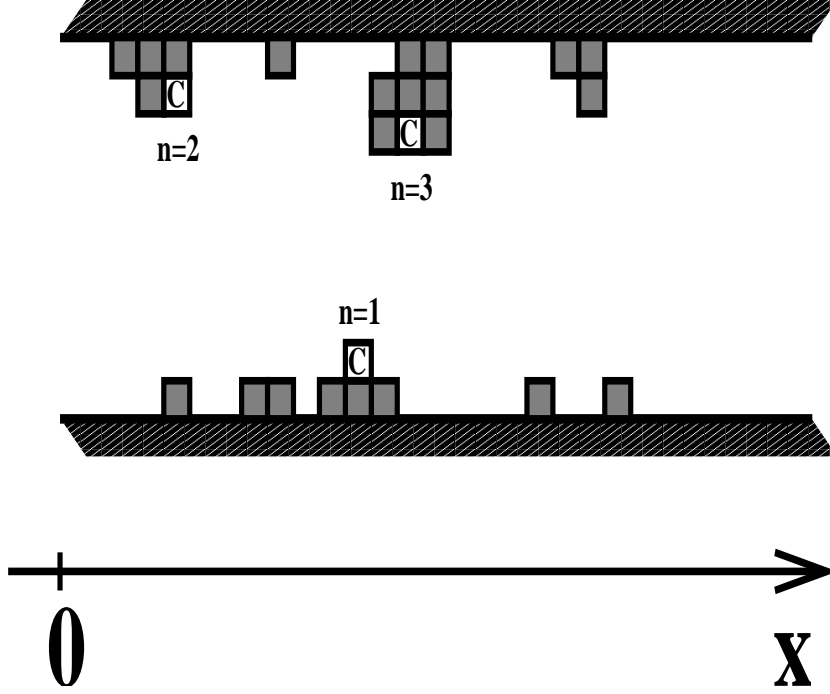

Fig. 3. Some possible aggregation positions for diffusing particles (empty squares with label C) with the corresponding numbers of nearest neighbors n.

In the first aggregation rule, hereafter called rule I,

$$p_{ag} \equiv p^{(4-n)}. \tag{1}$$

In our simulations, we will consider the cases $p = 0.1$ and $p = 0.05$. The value of the parameter p is the aggregation probability for a particle C with three aggregated neighbors. With the above values of p, p_{ag} rapidly increases with n: $p_{ag} \sim 10^{-2}$ with two neighbors and $p_{ag} \sim 10^{-3}$ with one neighbor. Thus, while aggregation to a flat surface is very difficult ($p_{ag} \sim 10^{-3}$), it is much easier at irregular regions of the deposit, in which the diffusing particle may encounter two or three neighbors.

In the second aggregation rule, hereafter called rule II,

$$p_{ag} \equiv 1 - q^{n}. \tag{2}$$

The values $q = 0.99$ and $q = 0.995$ will be considered in our simulations. This aggregation rule represents a much slower decrease of p_{ag} when n decreases; typically, p_{ag} doubles from $n = 1$ to $n = 2$ and increases 50% from $n = 2$ to $n = 3$. Rule II may represent the effects of adsorption and subsequent

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desorption of a particle C when it is near the solid deposit. In this case, the parameter q is of order $\exp\left(-E/k_BT\right)$, where E is an activation energy and T is the temperature.

For any set of the model parameters, the average values were taken over 100 to 1000 realizations.

DLA with aggregation rules similar to rule I (Eq. 1) were previously analyzed by various authors [15,16], leading to a crossover from compact to ramified clusters. DLA models in striped geometries were previously studied in Ref. [17], but the aggregation probabilities were independent of the number of neighbors (the usual condition) and the particle flux was very different from that considered here.

3   Results

First we discuss the results obtained for Knudsen diffusion, i. e. with ballistic motion of species C inside the pore. There is no bias in this case.

In Fig. 4a we show a sequence of configurations of the deposit inside a pore of width $W = 40$, obtained in simulations of rule I with $p = 0.1$. In Fig. 4b we show a sequence of configurations obtained in simulations of rule II with $q = 0.99$. Due to the probabilistic nature of the process, there are height fluctuations around any position x along the pore. There is an initial period of uniform deposition. Subsequently, if the height is averaged over lengthscales of order W or larger, in both cases this average value decreases with x. At those lengthscales, the deposit has an approximately wedge shape, deviating from this form only near the entrance when the pore is almost plugged. At this critical regime, the coke concentration near the entrance increases much faster than at the inner part of the pore. Also notice that the deposits obtained with rule I are compact, while the deposits obtained with rule II have a ramified structure.

For other values of parameters p and q, similar results were obtained. In any case, the pores plug at their entrances, as expected from the mechanism of particle injection at that region. Indeed, higher coke concentrations at the external surface of catalyst particles (pellets) is experimentally observed in several situations [10,11]. However, before discussing other nontrivial features of the Knudsen diffusion model, we will show that similar results are obtained in the molecular diffusion regime, even with a small bias along the pore.

For the molecular diffusion model, several values of v were considered (typically between $v = 0$ and $v = 10.0$) for each value of parameters p (aggregation
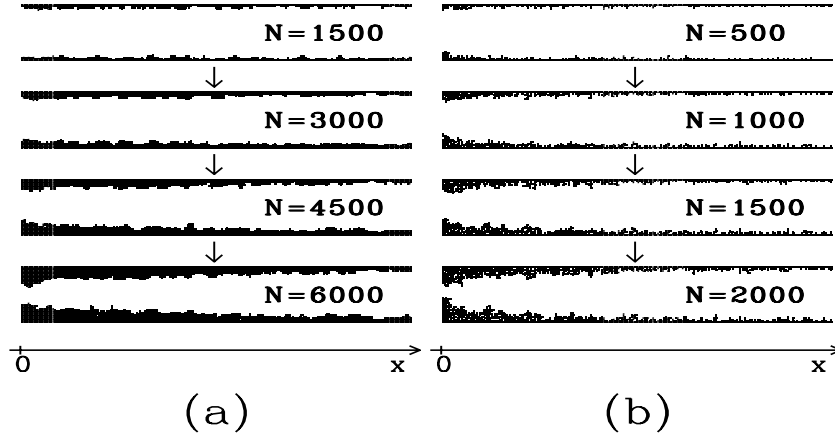
Fig. 4. Sequence of configurations of the left side of a pore with $W = 40$ for Knudsen diffusion: (a) aggregation rule I with $p = 0.1$; (b) aggregation rule II with $q = 0.99$. The number of deposited particles of each configuration, N, is indicated.

rule I) and q (rule II). Small v represents weak diffusional bias, while large v represents a rapid flux along the pore, with rare collisions with its surface. Large v is certainly not a realistic description of real catalytic processes, but it was also analyzed for completeness.

In Fig. 5a we show a sequence of configurations of a pore of width $W = 40$, obtained in simulations of rule I with $p = 0.1$ and $v = 0.1$. In Fig. 5b we show a sequence of configurations of the same pore using rule II with $q = 0.99$ and $v = 0.2$. We also observe the decrease of the average height of the deposit along the pore at lengthscales of order W or larger, which is confirmed for the other values of p and q and small v.

When the diffusional bias v along the pore increases, the typical morphology of the deposit changes, showing much larger heights' fluctuations. The pore plugs at positions far from $x = 0$ and the approximately wedge shape of the deposit disappears.

In order to analyze quantitatively the conditions of pore plugging in the molecular diffusion model, we calculated the average horizontal position $\langle x_p \rangle$ at which the pores become plugged, i. e. the average position of the last aggregated particle. In Fig. 6a we show $\langle x_p \rangle$ versus the bias v for aggregation rule I, with two values of p and three different widths. In Fig. 6b we show $\langle x_p \rangle$ versus v for aggregation rule II, with two values of q, for $W = 20$ and $W = 40$.
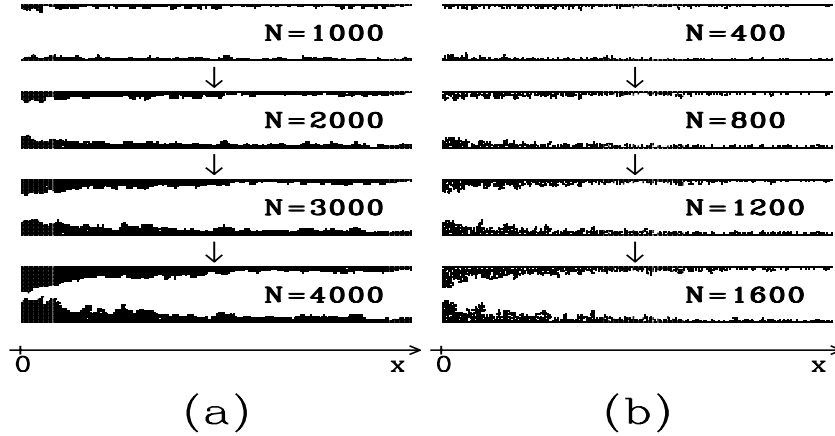
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Fig. 5. Sequence of configurations of the left side of a pore with $W = 40$ for particles executing biased molecular diffusion: (a) aggregation rule I with $p = 0.1$ and $v = 0.1$; (b) aggregation rule II with $q = 0.99$ and $v = 0.2$. The number of deposited particles of each configuration, N, is indicated.

In all cases, there is a range of small v in which $\langle x_p \rangle$ is significantly smaller than the widths W: $v \leq 0.02$ for rule I with $p = 0.1$ and $p = 0.05$, $v \leq 0.1$ for rule II with $q = 0.99$ and $q = 0.995$. It indicates plugging at the pore mouth, which is confirmed by visual inspection of various pore configurations (see, for instance, Figs. 5a and 5b). The qualitative features of the deposits with no bias $v = 0$ are the same (saturation of $\langle x_p \rangle$ at a small value).

Now we consider some quantitative properties of the deposits generated by both diffusion models.

One of the parameters that characterize the shape of the deposits is the average horizontal position of aggregation, $\langle x_{ag} \rangle$, which is the position of the center of mass relative to the entrance. This quantity is useful for describing their coarse grained features, independently of local thickness fluctuations. $\langle x_{ag} \rangle$ was measured as a function of the number of deposited particles N, which is proportional to the mass of the deposit.

In Fig. 7 we show $\langle x_{ag} \rangle / W$ as a function of N for the model of Knudsen diffusion with both aggregation rules. Average values were taken only over the set of configurations which were not blocked. Moreover, Fig. 7 shows only data for values of N in which more than 50% of the pores were not blocked. Consequently, they represent the growth regime of the deposits but not the
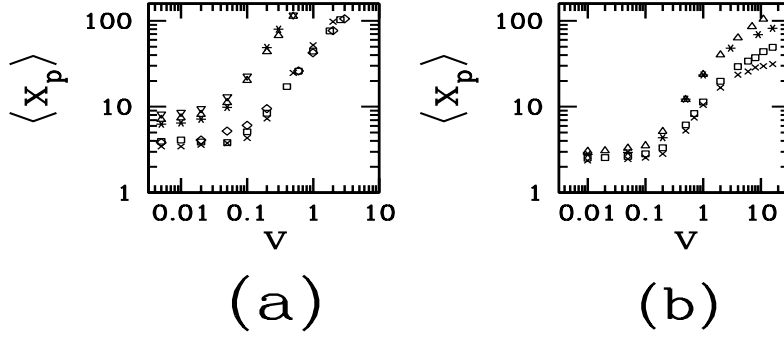
Fig. 6. Average horizontal position at which the pores plug, $\langle x_p \rangle$, as function of the diffusional bias v, for the molecular diffusion model. (a) Aggregation rule I with: $p = 0.1$ and $W = 10$ (diamonds), $W = 20$ (squares) and $W = 40$ (crosses); $p = 0.005$ and $W = 10$ (down triangles), $W = 20$ (up triangles) and $W = 40$ (asterisks). (b) Aggregation rule II with: $q = 0.99$ and $W = 20$ (squares) and $W = 40$ (crosses); $q = 0.995$ and $W = 20$ (triangles) and $W = 40$ (asterisks).

critical pore blocking.

Two regimes are observed in Fig. 7. The deposition initially occurs in a large region of the pore and not only at its entrance - the entrance is typically the region with $\langle x_{ag} \rangle / W < 1$. Subsequently, the deposit becomes large, with significant thickness fluctuations that reduce the effective diffusivity and makes it easier for particles C to aggregate to the irregularities of the surface. Consequently, $\langle x_{ag} \rangle$ slowly decreases with N. The results for both models indicate a decay $N^{-\beta}$, with $\beta \sim 0.25$, as illustrated in Fig. 7. This relation is just an effective form of decay for restricted ranges of N, since the local slopes of the curves in Fig. 7 have significant fluctuations in the regime of $\langle x_{ag} \rangle$ decay (mainly for model II). For finite and small widths, as expected in catalyst pores, this limitation in the range of N is natural. Consequently, that form of decay may not be interpreted as an universal scaling law for such processes within the expected limits of application.

In Fig. 8, we show the results for the molecular diffusion model in the small v regime.

In the case of aggregation rule I, the evolution of $\langle x_{ag} \rangle$ is similar to that of
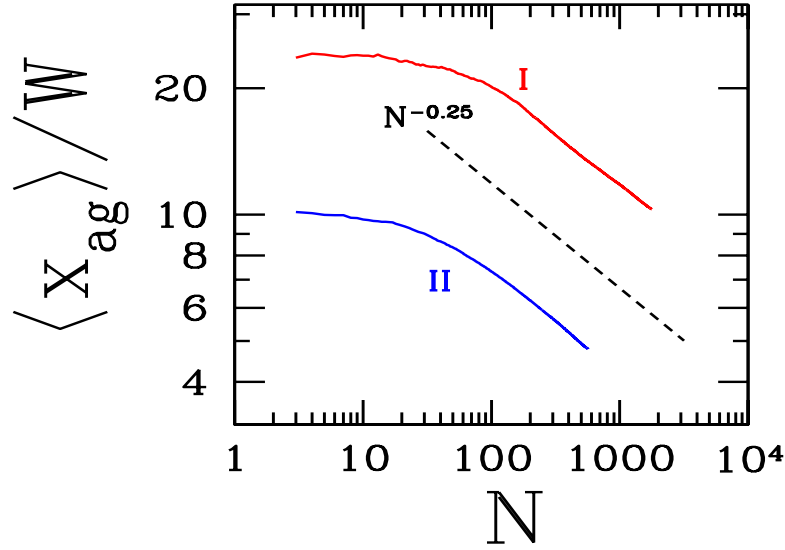
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Fig. 7. Ratio between the average horizontal position of aggregation $\langle x_{ag} \rangle$ and the pore width W as a function of the number of deposited particles N, for the model of Knudsen diffusion: aggregation rule I with $W = 20$ and $p = 0.1$; aggregation rule II with $W = 20$ and $q = 0.99$. The dashed line illustrates the decay as $N^{-0.25}$.

the Knudsen model, also including a decay with $\beta \sim 0.25$ for large deposits. For much smaller bias (including $v = 0$), the values of $\langle x_{ag} \rangle$ are much smaller and its decrease is slower, which corresponds to effective exponents β slightly smaller ($\beta \sim 0.15$). For aggregation rule II, with a relatively large bias, $\langle x_{ag} \rangle$ also decays very slowly until the pore blocking regime. This is an effect of the weak dependence of p_{ag} on the number of aggregated neighbors n for this rule (see Sec. II) and of the biased diffusion, both reducing the influence of the irregularities on the aggregation process.

The above results show that, in the model of Knudsen diffusion, which is expected to be more adequate for real catalytic processes, the deposits generated by diffusion and aggregation of particles entering the pore have some features which do not depend on the details of the aggregation conditions. For small deposits, the assumption of a uniform coke profile ($\langle x_{ag} \rangle \approx const$) is reasonable; indeed this approximation is frequently adopted in continuum models. However, as the deposit becomes larger, neither the uniform profile nor the assumption of a wedge-shaped deposit of constant slope [4,8,9] is supported by our microscopic models. The wedge-shaped deposit of constant slope would correspond to a linear increase of $\langle x_{ag} \rangle$ with N, in contrast to the decrease shown in Figs. 7 and 8. Instead, the assumption of the above effective $N^{-\beta}$ law with small β ($\beta \sim 0.25$ for Knudsen diffusion) seems to be a better approximation and might eventually be tested in continuous models.
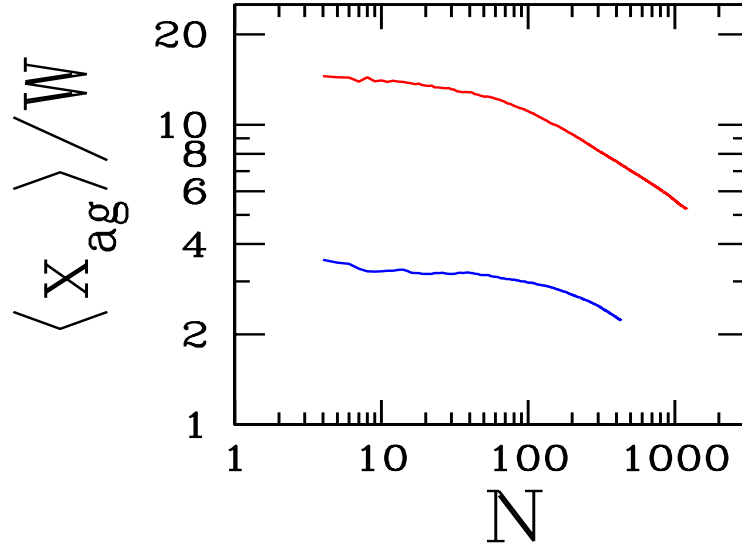
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Fig. 8. Ratio between the average horizontal position of aggregation $\langle x_{ag} \rangle$ and the pore width W as a function of the number of deposited particles N, for the molecular diffusion model with small bias: aggregation rule I with $W = 20$, $p = 0.1$ and $v = 0.05$ (top curve); aggregation rule II with $W = 20$, $q = 0.99$ and $v = 0.2$ (lower curve).

4   Conclusion

We presented results of simulations of various models of transport and aggregation of a single species in isolated pores in order to represent the basic mechanisms of coke deposition in catalyst pores. In the first model, representing the Knudsen regime, the diffusing species (particles C) executed ballistic motion between collisions with the pore walls or with the deposit. In the second model, suitable for the molecular diffusion regime, the C particles executed biased random walks inside the pores. Two probabilistic rules for aggregation to the walls or to the deposit were considered, leading to dense or ramified deposits.

In the Knudsen diffusion model or in the molecular diffusion case with weak bias along the pore, the deposits formed at the pore surface have approximately wedge shapes at lengthscales of order W or larger. Consequently, the pore plugging occurs at the pore mouth. The average position of aggregation slowly decreases with the number of particles, approaching the pore mouth ($x = 0$) as the deposit becomes larger. These results for Knudsen diffusion do not depend on the details of the aggregation mechanisms. An effective decay $\langle x_{ag} \rangle \sim N^{-0.25}$ is obtained after a transient regime of uniform deposition and

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before the critical regime of pore plugging. Similar results are found in some conditions of the molecular diffusion models with small bias. Consequently, the hypothesis of uniform coke profiles along the pores [6,7] and the hypothesis of a wedge-shaped deposit of constant slope [4,8,9], frequently adopted in continuous reaction-diffusion models during the whole deposition period, are not supported by our microscopic models.

Those models were not designed to describe quantitatively any real catalyst because our interest was to analyze some general features of the deposits inside the pores. On the other hand, since very different conditions of diffusion and aggregation were considered, our results suggest that the above features are not consequences of a particular model. Instead, they are general conclusions that follow from the assumption that coke deposition is a consequence of diffusion-limited aggregation of carbonaceous residues inside catalyst pores. Thus, we expect that the information obtained from our study can be applied to other processes, possibly of technological interest. For instance, in models with prior assumptions of the shapes of coke profiles, the approximate dependence of $\langle x_{ag} \rangle$ on the mass of the deposit might be tested. The extension for modeling coke deposition in a specific catalyst system would also include the description of diffusion and chemical reactions of several species inside the pores, as well as considering their connectivity.

Acknowledgements

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